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SYNTHESIS, STEREOCHEMISTRY, AND CIRCULAR DICHROISM OF OPTICALLY ACTIVE *o*-SUBSTITUTED DIPHENYL SULPHILIMINES AND RELATED COMPOUNDS[1]

MASARU MORIYAMA and TOSHIAKI YOSHIMURA
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

and

NAOMICHI FURUKAWA, TATSUO NUMATA and SHIGERU OAE*
Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

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Abstract—Optically active *o*-substituted diphenyl N-substituted sulphilimines are readily synthesised by the reaction of the corresponding sulphides and t-butyl hypochlorite in the presence of *l*-menthol and amide anions. (−)-N-*p*-Tolylsulphonylsulphilimines (**1**, **2**) obtained were converted to the corresponding (−)-N-unsubstituted sulphilimines (**8**, **9**) by treating them with concentrated sulphuric acid. When (−)-S-*o*-anisyl S-phenyl N-(unsubstituted) sulphilimine (**8**) was treated with acylating agents or acrylonitrile, the corresponding optically active (−)-N-substituted sulphilimines were prepared with complete retention at sulphur. The absolute configuration of (−)-S-*o*-anisyl S-phenyl N-*p*-tolylsulphonylsulphilimine (**1**) was determined by converting it to (+)-S-*o*-anisyl sulphoxide (**17**). CD curves of (−)-*o*-substituted diarylsulphilimines exhibited a negative Cotton effect at around 270–285 nm, which was assigned to (*S*)-configuration at sulphur by comparing with the analogous sulphoxides. The substituent on the imino group of the sulphilimine gave no appreciable effect on the CD behavior and the lack of substituent effect was considered to be due to the semi-polar character of the S(IV)-N bond. Unusual effect of *o*-methoxy group on the CD curves was discussed in connection with solvent effect. Mechanism of this asymmetric synthesis has been investigated, and it has become apparent that the diastereomeric menthoxysulphonium chloride was an excess of (*RR*)-configuration was formed initially and the amide anion attacks the S atom of the salt with net inversion.

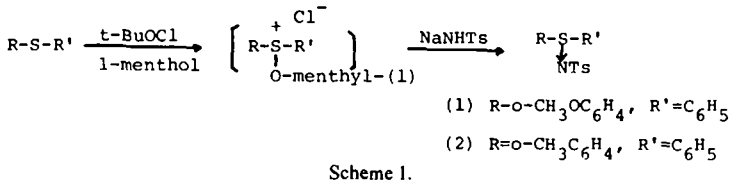
Although useful procedures have been reported for the preparation of N-substituted sulphilimines such as N-sulphonyl-,[2] N-acyl-,[3] N-alkyl-,[4] N-aryl-,[5] N-ethoxycarbonyl-,[6] N-carbamoyl-,[7] N-cyano-,[8] N-halo-[9] and N-unsubstituted (free) sulphilimines,[10,11] no routine route to prepare the optically active sulphilimines has been found. Cram *et al.* reported a synthetic method of optically active S-methyl S-*p*-tolyl N-*p*-tolylsulphonylsulphilimine by treating the corresponding optically active sulphoxide with N-sulphinyl *p*-tolylsulphonylamide (or N,N′-bis(*p*-tolylsulphonyl)sulphurdiimide) in high stereospecificity.[12] However, this procedure has not been extended for the preparation of optically active diaryl N-*p*-tolylsulphonylsulphilimines or other N-substituted sulphilimines.[13] We reported previously that a variety of free sulphilimines are readily prepared by treating the corresponding N-*p*-tolylsulphonylsulphilimines with conc. sulphuric acid.[10] Furthermore, various N-substituted sulphilimines have been prepared by either alkylation or acylation of the diaryl free sulphilimines with a variety of appropriate electrophilic reagents.[10,14] Therefore, if there is any simple way to prepare optically active diaryl N-*p*-tolylsulphonylsulphilimines, it will become an important procedure to synthesize various optically active N-substituted diaryl sulphilimines.

Meanwhile, the absolute configurations of the sulphilimines need clarification since the only two reported concerning with ORD measurements of optically active alkyl aryl N-*p*-tolylsulphonylsulphilimines and S-methyl S-*p*-tolyl N-*p*-tolylsulphonylsulphoximine.[12,15] Hence, CD studies on newly made optically active sulphilimines and sulphoximines, were carried out, since the CD curve would be most helpful in determining the optically active transition of each step of the reactions involved.

This paper deals with not only the synthesis and CD studies of *o*-substituted diaryl sulphilimines and sulphoximines, but also the mechanism of the reactions.

RESULTS AND DISCUSSION

N-Substituted sulphilimines. Optically active S-*o*-anisyl S-phenyl-(**1**) and S-phenyl S-*o*-tolyl N-*p*-tolylsulphonylsulphilimine (**2**) were synthesised by treating the corresponding sulphide and t-butyl hypochlorite in accordance with Scheme 1. The reaction appears to proceed via an initial formation of diastereomeric (*l*)-menthoxysulphonium chloride which reacts further with tosylamide anion affording the optical active sulphilimines. Although the menthoxysulphonium salt was not isolated during the reaction, its formation was confirmed as the perchlorate salt upon prior treatment of the mixture of the sulphide, t-butyl hypochlorite and *l*-menthol with sodium perchlorate before mixing the mixture with tosyl amide anion. Thus, the menthoxysulphonium salt should be the key intermediate for the asymmetric induction (Scheme 1). The specific rotation of the sulphilimine thus obtained increased by the repeated recrystallizations from acetone-hexane and reached finally a constant value. If we assume the value of $[\alpha]_D$ for **1**, −98.0 to be of 100% optical pure, the asymmetric induction in the synthesis of the sulphilimine by *l*-menthol should be around 20–30%. Analogously, other S-*o*-anisyl S-phenyl N-arylsulphonylsulphilimines were also prepared (Table 1). Interestingly, N-(*p*-substituted)-phenylsulphonylsulphilimines (**1**, **2**, **3**, **4**) increased their



(1) R-o-$CH_3OC_6H_4$, R'=C_6H_5

(2) R=o-$CH_3C_6H_4$, R'=C_6H_5

Scheme 1.

Table 1. S-*o*-Anisyl S-phenyl N-substituted sulphilimines, *o*-CH_3O-C_6H_4-S-C_6H_5 (NX)

X		$[\alpha]_D$[a]	M.p.(°C)	Yield(%)[b]	Phase[c]	Method[d]
p-$CH_3C_6H_4SO_2$	(1)	- 31.9	155 -159	62	M	A
		- 98.0	161.5 - 162.0	15		B
		- 23.5	-	65		C
p-$ClC_6H_4SO_2$	(3)	- 28.3	154.0 - 155.5	60	M	A
		- 78.2	160.5 - 161.0	12		B
p-$CH_3OC_6H_4$	(4)	- 19.5	142 - 143	20	M	A
		- 88.7	149.5 - 150.5	2		B
$C_6H_5SO_2$	(5)	- 20.0	-	62	C	C
		- 2.7	143.5 - 144.0	42		D
		- 79.3	-	3		E
o-$CH_3C_6H_4SO_2$	(6)	- 4.9	153 - 154	45	C	D
		- 49.1	149 - 152	6		E
C_6H_5CO	(7)	- 13.0	-	65	C	C
		- 1.2	118 - 119	50		D
p-$CH_3C_6H_4SO_2$[e]	(2)	- 15.5	102 - 103	48	M	A
		- 41	122.0 - 122.5	11		B

a) Determined in chloroform (c= 1.0). b) By-product was the corresponding sulphoxide.
c) M: Racemic mixture. C: Racemic compound.
d) See Experimental section. A: Recrystallised one time. B: Recrystallised two or three times. C: Chromatographed only. D: Chromatographed and recrystallised. E. Recrystallised again from filtrate of method D.
e) S-o-tolyl S-phenyl N-p-tolylsulphonylsulphilimine.

optical purities by repeated recrystallisations, while those of N-(*p*-unsubstituted)-phenylsulphonylsulphilimines (**5**, **6**) decreased. In the latter, the specific rotations of the oil obtained by evaporation of solvent from the filtrates were larger than those of the crystals.

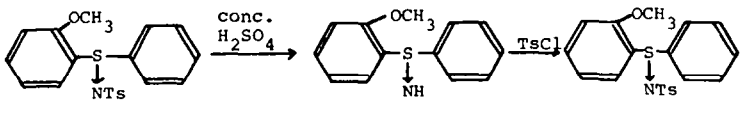
S-*o*-Anisyl S-phenyl N-benzoylsulphilimine (**7**) was prepared similarly by treating the corresponding menthoxysulphonium chloride with sodium benzamide.

Since these sulphilimines are obtained in high optical purities by simple recrystallization, this method is a useful procedure for preparating various optically active *o*-substituted diphenyl sulphilimines. The results are shown in Table 1.

N-*Unsubstituted (free) sulphilimines.* When optically active N-*p*-tolylsulphonylsulphilimines (**1**, **2**) were treated with conc sulphuric acid, the corresponding optically active free sulphilimines (**8**, **9**) were obtained in relatively good yields. However, upon recrystallization of the partially optically pure free sulphilimine (**8**) ($[\alpha]_D$ −108°) from benzene-hexane, the crystals obtained had a lower specific rotation ($[\alpha]_D$ −64.1) than the oil obtained by evaporation of the solvent from the filtrate ($[\alpha]_D$ −141°) (Table 2). Accordingly, the compound having higher optical purity is easily accesible from the lower one by recrystallization like the N-substituted sulphilimines.

The signs of rotations of both free sulphilimines (**8**, **9**) are identical and the magnitudes of the molecular rotations do not vary significantly as compared to those of the starting N-*p*-tolylsulphonylsulphilimines (**1**, **2**) as shown in Table 3. Assuming that the substituents on the N atom do not have any large influence on the optical activity of the asymmetric sulphur species, the above results suggest that the N-S(IV) bond cleavage in conc. sulphuric acid proceeds with retention at S (III) atom and the corresponding intermediate, i.e. the aminosulphonium salt, does not racemise under the reaction. This situation was confirmed by the experiment shown in Scheme 2.

Namely, the specific rotation of the resulting N-*p*-tolylsulphonylsulphilimine (**1**) was identical both in sign and in magnitude with that of the starting material. Thus,



(1) (8) (1)

$[\alpha]_D$ -98° $[\alpha]_D$ -194° $[\alpha]_D$ -98°

Scheme 2.

Table 2. N-Unsubstituted sulphilimines,

$$o\text{-Y-C}_6\text{H}_4\text{-H}_4\text{-S-C}_6\text{H}_5 \xrightarrow{\text{conc } H_2SO_4} o\text{-Y-C}_6\text{H}_4\text{-S-C}_6\text{H}_5$$

$$\downarrow \qquad\qquad \downarrow$$

NTs (1, 2) NH (8, 9)

Y		$[\alpha]_D$[a] Substrate	Product	Yield(%)[b]	M.p.(°C)	Method[c]
CH_3O	(8)	- 98	-194	57	-	A
		- 55	-108	62	-	A
			- 64.1	28	91 - 93[d]	B
			- 141	30	-	C
CH_3	(9)	- 41	- 85	70	-	A

a) Determined in chloroform (c=∼1.0).
b) Yield from the starting N-p-tolylsulphonylsulphimide.
c) See Experimental section.
A: Removed benzene. B: Recrystallised from product of method A ($[\alpha]_D$ -108°). C: Removed solvent from the filtrate of method B.
d) The racemic free sulphimide(8) melts at 96-97°C.

Table 3. Molecular rotation of *o*-substituted diphenyl sulphilimines and sulphoximines,[a] *o*-Yo-C_6H_4-S-C_6H_4-W-p

↓ Z

Y	Z	W		$[M]_D$
OCH_3	NTs	H	(1)	- 377°
OCH_3	NH	H	(8)	- 448°
OCH_3	O	CH_3	(10)	- 482°
CH_3	NTs	H	(2)	- 151°
CH_3	NH	H	(9)	- 183°
CH_3	O	CH_3	(11)	- 168°

a) Determined in chloroform (c=∼1.0).

the free sulphilimine (**8**) ($[\alpha]_D$ −194°) derived from the optically pure sulphilimine (**1**) ($[\alpha]_D$ −98°) should have 100% optical purity.

Moreover, the similar magnitudes of molecular rotations between the sulphilimines (**1, 8, 2, 9**) and the corresponding isoelectronic sulphoxides (**10, 11**) suggests both the imino groups (NH, NTs) and oxygen attached to the S atom to have similar effects upon the cause of the optical activities (Table 3).[16] This was also confirmed by the CD studies as will be described later. In addition, since the signs of optical rotations of these sulphilimines (**1, 2, 8, 9**) are identical to those of the corresponding (−)-(*S*)-sulphoxides (**10, 11**) of the known absolute configuration,[17,18] they are considered to have (*S*)-configuration around sulphur.

These are the first examples of stable optically active free sulphilimines to be synthesized; the rate constant of thermal racemisation of the free sulphilimine (**8**) was 2.22×10^{-5} sec^{-1} (in chloroform, at 75°) under dry N_2 atmosphere.[19] Therefore, this method is a useful and convenient procedure to prepare optically active free sulphilimines.[20]

N-Substituted sulphilimines from the (−)-free sulphilimine (**8**). Optically active N-acyl- and N-arylsulphonylsulphilimines were obtained easily by the reactions of the (−)-free sulphilimine (**8**) with carboxylic anhydride and arenesulphonyl chloride, respectively. (−)-N-β-Cyanoethylsulphilimine (**15**), a kind of N-alkyl sulphilimine was also prepared by treatment of (−)-free sulphilimine (**8**) with acrylonitrile at room temperature. The results of these conversions are summarized in Table 4.[10,14]

These reactions are considered to proceed with complete retention at the S atom, since both acylation and alkylation occur at the N atom without breaking any bonds attached to the chiral S atom. This was actually found to be the case for the reaction sequence shown in Scheme 2.

These results demonstrate that the reaction described above is a useful procedure for preparation of a variety of optically active N-substituted sulphilimines.

Conversion of the (−)-free sulphilimine (**8**) *to the (+)-sulphoximine* (**16**) *and the (+)-sulphoxide* (**17**). When the (−)-free sulphilimine (**8**) was oxidised with $KMnO_4$-$MgSO_4$, the optically active (+)-N-unsubstituted (free) sulphoximine (**16**) was obtained in a good yield. Moreover, the (+)-free sulphoximine (**16**) was converted quantitatively to (+)-S-*o*-anisyl S-phenyl sulphoxide (**17**) upon treatment with nitrous acid. The configuration of **17** has not been determined, however (−)-S-*o*-anisyl, S-*p*-tolyl sulphoxide is determined as of (*S*)-configuration.

Assuming that the *p*-Me group has no significant influence on the optical activity,[16] the (+)-sulphoxide (**17**) is considered to be almost pure optically, since the magnitudes of the molecular rotations of the sulphoxide (**17**) (+638) and of optically pure **10** (−637) in acetone are nearly identical. The positive sign of the former compound (**17**), also indicates that the compound has (*R*)-configuration around S atom.

It is well known that the oxidation (sulphilimine to sulphoximine) and deimidation (sulphoximine to sulphoxide) reactions proceed with complete retention of configuration at sulphur.[12,15] Thus, inspection of the reaction sequence summarised in Scheme 3 reveals that the starting (−)-N-*p*-tolylsulphonylsulphilimine (**1**) has (*S*)-configuration at sulphur. In summary, all the reactions, i.e. (−)-N-*p*-tolylsulphonylsulphilimine (**1**) to (−)-free sulphilimine (**8**) (−)-(**8**) to (+)-free sulphoximine (**16**), and (+)-(**16**) to (+)-sulphoxide (**17**) proceed with nearly complete retention.

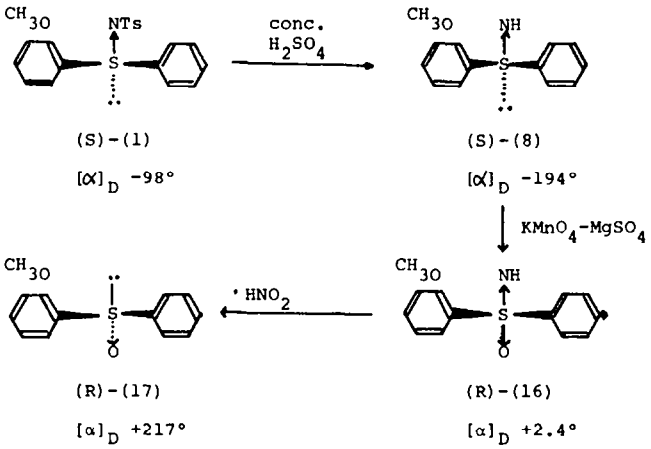
CD Behaviors of the (−)-free sulphilimine (**8**), *the (−)-sulphoxide* (**10**), *and the (+)-sulphoxide* (**17**). The UV spectra and CD curves for the (−)-free sulphilimine (**8**) and the (+)-sulphoxide (**17**) are depicted in Fig. 1 together with those for the (−)-sulphoxide (**10**) of a known absolute configuration (*S*).[22] The CD curves of the two sulphoxides

Table 4. N-Substituted sulphilimines from the free sulphilimine (8).

$$o\text{-}CH_3O\text{-}C_6H_4\text{-}S\text{-}C_6H_5 \xrightarrow{\text{Reagent}} o\text{-}CH_3O\text{-}C_6H_4\text{-}S\text{-}C_6H_5$$
$$\text{(8)} \quad \downarrow \text{NH} \qquad\qquad \downarrow \text{NX}$$

X		Reagent	Substrate	Product	Yield(%)	M.p.(°C)	Phase[b]	Method[c]
CH_3CO	(12)	$(CH_3CO)_2O$	-107	- 86.2	77	-	C	A
				- 74.0	45	120 - 122		B
C_6H_5CO	(7)	$(C_6H_5CO)_2O$	-107	- 43.6	83	-	C	A
				- 40.5	48	97 - 99		B
			-194	- 76	55	99 - 99.5		B
$(CH_3)_2CHCO$	(13)	$((CH_3)_2CHCO)_2O$	-157	-123	76	-	M	A
				-145	38	81 - 83		B
CF_3CO	(14)	$(CF_3CO)_2O$	-157	- 66.7	77	-	C	A
				- 61.3	27	54 - 56		B
$p\text{-}CH_3C_6H_4SO_2$	(1)	$p\text{-}CH_3C_6H_4SO_2Cl$	-194	- 98	95	-	M	A
$C_6H_5SO_2$	(5)	$C_6H_5SO_2Cl$	-157	- 77	93	-	C	A
CH_2CH_2CN	(15)	CH_2=CHCN	-138	- 96	65	-	M	A
				-135	10	75 - 76[d]		B

a) Determined in chloroform (c= 1.0).
b) M: Racemic mixture. C: Racemic compound.
c) See Experimental section. A: Chromatographed only. B: Chromatographed and recrystallised.
d) The racemic sulphilimine(15) melts at 58-59°C.



Scheme 3.

are practically mirror images of one another. Therefore, this CD measurements support the conclusion that the absolute configuration of the sulphoxide (**17**) is (*R*) and that the *p*-Me group has very little influence on the optical activity.[16]

Like both sulphoxides (**10**, **17**), the UV spectrum of the free sulphilimine (**8**) has a shoulder at 225 nm (ϵ = 12,100) and a maxima at 283 nm (ϵ = 3890), and both transitions are due to the optical activities. Moreover, the resemblance of CD curves both in shape and sign of their Cotton effects serve as evidence to support that the absolute configurations of these two compounds (the (−)-sulphoxide (**10**) and the (−)-free sulphilimine (**8**)) are identical (*S*).[20] These UV and CD data indicate that the substitution of the O atom by the imino group at the S atom does not change the electronic transitions which are mainly responsible for the CD behavior. Thus, this implies that the S–N bond character in the free sulphilimine (**8**) is of a semi-polar nature like that of the S–O bond in the corresponding isoelectronic sulphoxide (**17**).[23]

CD Behavior of (−)-N-*substituted sulphilimines.* The CD and UV curves of typical (−)-N-substituted sulphilimines, i.e. (−)-S-*o*-anisyl S-phenyl N-*p*-tolylsulphonyl (**1**), N-benzoyl (**7**)-, and N-β-cyanoethylsulphilimines (**15**) are displayed in Fig. 2, and those for other N-substituted sulphilimines are listed in Table 5. These sulphilimines bearing an *o*-OMe group, exhibit CD curves similar to the corresponding (−)-(*S*)-free sulphilimine (**8**) except for larger amplitudes of the Cotton effects near 283 nm. The close similarity of their CD behavior supports the previous conclusion that these (−)-N-substituted sulphilimines possess the same configuration (*S*) at sulphur.

The correlation between the CD and UV pattern is interesting. While the N-*p*-tolylsulphonylsulphilimine (**1**) absorbs at 288 nm (ϵ = 3880) and 229 nm (ϵ = 15,500), N-β-cyanoethylsulphilimine (**15**) has only one absorption band at 287 nm (ϵ = 4340). The more intense absorptions near 230 nm have been designated as the ^1L_a bands due to the phenyl rings attached to the N atom of the sulphilimine, since such an intense band is not present in the sulphilimine bearing no aromatic ring attached to the N. This was predicted earlier for various N-*p*-tolylsulphonylsulphilimines.[24] Consequently, though the

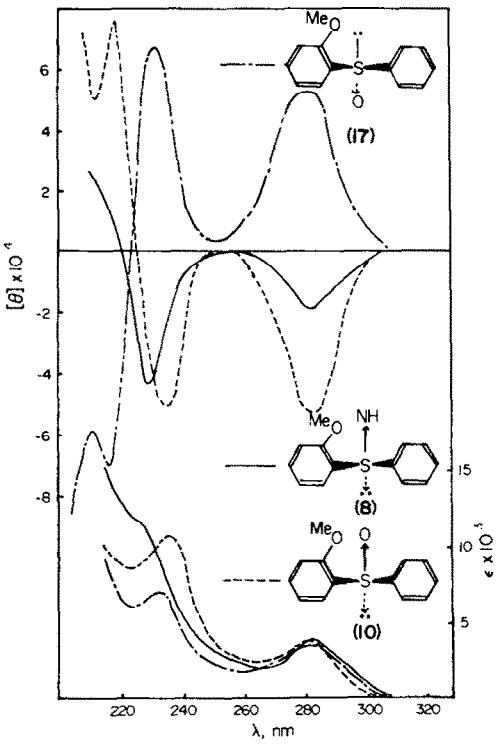


Fig. 1. Circular dichroism curves and ultraviolet spectra of (**8**), (**10**) and (**17**) in methanol.

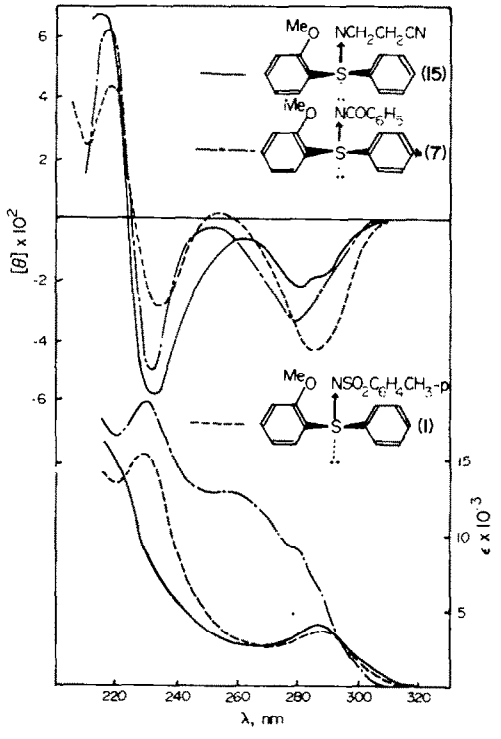


Fig. 2. Circular dichroism curves and ultraviolet spectra of (**1**), (**7**) and (**15**) in methanol.

Cotton effects, at a short wave length between 215 and 230 nm, can be correlated with coupling between the local benzene $\pi \rightarrow \pi^*$ (^1L_a) and sulphilimine $n \rightarrow \pi^*$ excitations, the corresponding absorption would be hidden behind the tail of the shorter wave length absorption band. The strong electron-withdrawing trifluoroacetyl group, however, might confuse such a coupling and hence the CD behavior of the N-trifluoroacetylsulphilimine (**14**) is different at 235 nm from those of other sulphilimines.

On the other hand, the less intense absorption bands at around 285 nm was observed in a similar manner for all the S-*o*-anisyl S-phenyl sulphilimines subjected to the CD measurements. Like diaryl sulphoxides, the absorption may result mainly from coupling between the ^1L_b bands of two aryl chromophores.[25]

In summary, it has become apparent that the substituent on the imino group of the sulphilimine does not give any appreciable effect, electronically (resonance) and sterically (relative disposition of the two aryl rings), on the inherently dissymmetric sulphilimine chromophore which is responsible for the characteristics of the CD properties. Once again, in view of the lack of resonance effect for the CD behavior, the S(IV)–N bond in the sulphilimine is considered to be an ylide-like semi-polar bond rather than covalent double bond.[24,26]

Effect of o-*substituent on CD curve.* (−)-S-Phenyl S-*o*-tolyl N-*p*-tolylsulphonylsulphilimine (**2**) shows a same negative Cotton effect centered around 270 nm ([θ] −17,000) with that of (−)-(S)-*o*-tolyl S-*p*-tolyl sulphoxide (**11**) ([θ] −19,700) as shown in Fig. 3. This similarity provides a reasonable basis for assigning (*S*)-configuration around the S atom of the (−)-sulphilimine (**2**).

The replacement of *o*-OMe group by Me group dramatically changes the shape of the CD curves of the sulphilimines (**1**, **2**). Namely, the *o*-Me derivative (**2**) has a smaller Cotton effect ([θ] −17,000) than that of the *o*-OMe derivative (**1**) ([θ] −43,300) at long wave length, and the former has no detectable Cotton effect in the region of short wave length at which the latter has strong Cotton effects ([θ] −29,700, [θ] +44,000). A similar fact was also observed for the corresponding sulphoxides (**10**, **11**) (Table 5). The high amplitudes of the Cotton

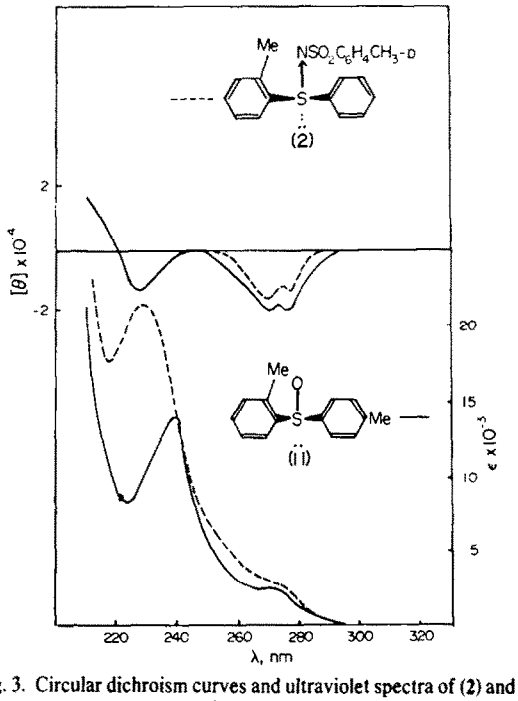


Fig. 3. Circular dichroism curves and ultraviolet spectra of (**2**) and (**11**) in methanol.

Table 5. Circular dichroism of *o*-substituted diphenyl sulphilimines, sulphoximines, and sulphoxides, *o*-CH_3O-C_6H_4-X-C_6H_5

X		Config.	Solvent[a]	C.d. characteristics, $[\theta] \times 10^{-3}$ (nm)[b]	U.v. characteristics, ε (nm)[c]
-S- ‖ NH	(-)-(8)	S	M	-19.2(283) -43.6(230) +16(215)*	3890(283) 12100(225sh)
			A	-20.0(282) -67.3(232) +56(210)*	3900(281) 11300(225sh)
			D	-21.0(280) -77.0(234) +49(215)*	4290(281)
			I	-24.5(279) -83.9(232) +65(215)*	4310(279) 13000(225sh)
-S- ‖ $NSO_2C_6H_4Cl$-p	(-)-(3)	S	M	-31.3(285) -20.5(233) +39(217)	3900(285) 22600(231)
			D	-38.0(284) -33.8(234) +49(217)	4060(285) 21800(232)
-S- ‖ $NSO_2C_6H_4OCH_3$-p	(-)-(4)	S	M	-39.1(285) -41.4(233) +65(217)	4760(282) 23700(235)
-S- ‖ $NSO_2C_6H_4CH_3$-p	(-)-(1)	S	M	-43.3(285) -29.7(235) +44(218)	3880(288) 15500(229)
-S- ‖ $NSO_2C_6H_5$	(-)-(5)	S	M	-32.8(285) -31.8(235) +47(218)	3920(288) 14400(225sh)
			D	-46.4(284) -45.2(233) +52(217)	4190(286) 18300(225sh)
-S- ‖ $NSO_2C_6H_4CH_3$-o	(-)-(6)	S	M	-[e] (285)	3870(288) 19400(225)
-S- ‖ $NCOCH_3$	(-)-(12)	S	M	-33.9(284) -31.4(233) +18(215)*	3600(282) 14600(225sh)
			D	-72.8(281) -94.9(230)	4290(282)
-S- ‖ $NCOC_6H_5$	(-)-(7)	S	M	-34.7(279) -51.6(232) +62(217)	9900(275sh) 12900(257) 18900(232)
-S- ‖ $NCOCH(CH_3)_2$	(-)-(13)	S	M	-41.8(284) -72.0(230) +35(218)	4100(287) 10300(225sh)
			D	-37.8(282) -54.5(231)	4300(283)
-S- ‖ $NCOCF_3$	(-)-(14)	S	M	-43.1(286) + 8.4(245) +28(223) - 4.9(235)	3700(288) 13800(225sh)
			D	-38.8(284) + 9.1(245) +34(220) - 9.1(234)	3780(287) 14800(225sh)
-S- ‖ NCH_2CH_2CN	(-)-(15)	S	M	-22.2(280) -58.2(232) +66(215)	4340(287)
-S- ‖ O	(+)-(17)	R	M	+52.4(283) +67.5(234) -71(218)	3700(284) 7200(234)
			D	+51.1(282) +90.0(235) -73(215)*	4020(281) 6300(234)
-S- ‖ O ‖ NH	(-)-(10)[d]	S	M[f]	-53.3(284) -51.5(236) +77(221)	4000(282) 10700(237)
			I	-45 (280) -117 (233) +100(215)	
-S- ‖ O	(+)-(16)	R	M	+ 8.3(283) + 4.0(233) -37(220) - 4.0(248)	3800(287) 13300(219)
			A	+ 3.0(285) + 5.3(234) -18(220) - 3.7(260)	3850(286) 13400(220)
			D	- 2.8(295) + 3.2(235) -13(223) - 4.5(268)	3860(286)
			I	- 0.9(295) + 4.5(233) -20(220) - 4.6(268)	3100(284)
NTs ‖ -S- ‖ O	(-)-(18)		M	+10.6(291) +10.0(237) -51(223) -20.8(250)	2550(292) 18700(225)
			D	+12.5(292) -231(223)	
-S- ‖ NTs	(-)-(2)[g]	S	M	-14.0(270)	3300(267sh) 21500(229)
			D	-18.3(271)	3400(267sh) 20200(230)
-S- ‖ O	(-)-(11)[h]	S	M	-19.8(277) -12.5(227) +18(210)*	2620(261sh) 14000(239)

a) Determined in (1.35-11.24) x 10^{-4} mole/l.
M: Methanol; A: acetonitrile; D: dioxane; I: isooctane.
b) Maximum molecular ellipticities are indicated and the wave lengths in parentheses.
*: Last reading. All values are corrected to optically pure.
c) Maximum molecular extinction coefficients are indicated and the wave lengths in parentheses.
sh: Shoulder.
d) S-o-Anisyl S-p-tolyl sulphoxide.
e) The optical purities could not be assigned.
f) The data obtained by Mislow et al..[22]
g) S-o-Tolyl S-phenyl sulphimide.
h) S-o-Tolyl S-p-tolyl sulphoxide.

effects for the *o*-OMe derivatives are probably caused by a large breakdown of symmetric property of the diaryl sulphilimine chromophore. Such an effect of the *o*-OMe group is probably due to either the steric compression of *o*-hydrogens by another phenyl group or the dipole-dipole interaction with the polar S(IV)–N group. Mislow *et al.* have observed an analogous phenomenon in the optical rotatory dispersion studies of (−)-(*S*)-S-*o*-tolyl S-*p*-tolyl (**11**) and (−)-(*S*)-S-mesityl S-*p*-tolyl sulphoxides.[17]

CD Behavior of the (+)-*sulphoximine* (**16**) *and* (−)-*sulphoximine* (**18**). Characteristic CD behavior of (+)-S-*o*-anisyl S-phenyl N-(unsubstituted) sulphoximine (**16**) and the corresponding (−)-N-*p*-tolylsulphonyl-sulphoximine (**18**) are quite interesting. Two small Cotton effects having opposite sign appear at 275 (and/or 240) nm and hence the rotational strengths are almost zero at these regions (Fig. 4). Moreover, in the case of the free sulphoximine (**16**), the small Cotton effect, appearing at long wave lengths, is markedly sensitive to solvent polarity. In polar solvents, its Cotton effect

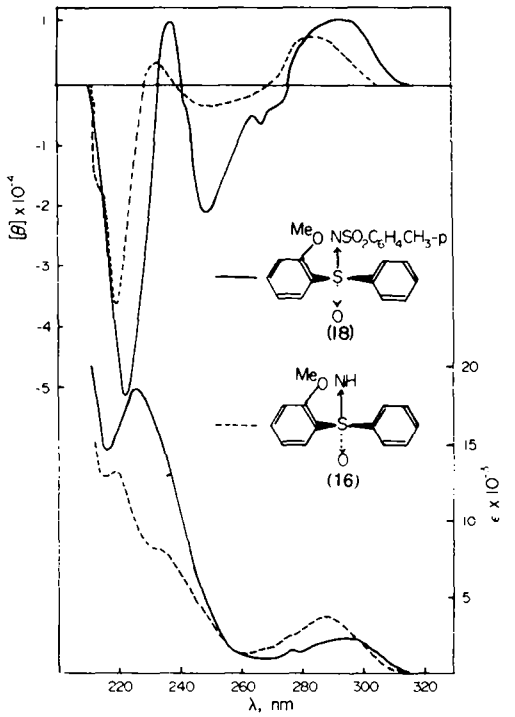


Fig. 4. Circular dichroism curves and ultraviolet spectra of (**16**) and (**18**) in methanol.

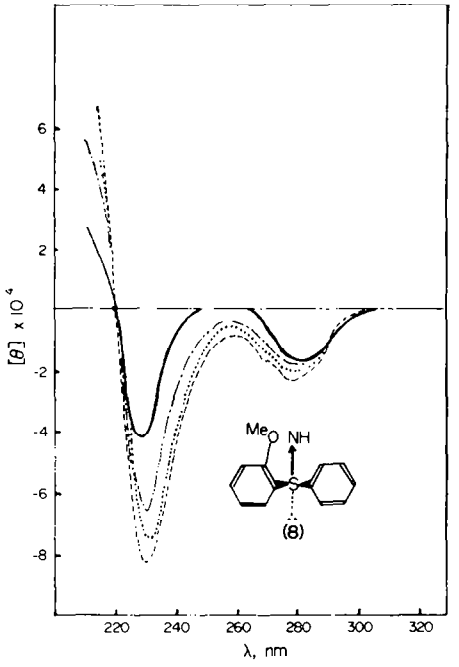


Fig. 5. Circular dichroism curves of (**8**) in methanol, acetonitrile, dioxane and isooctane. ——, methanol; – – – –, acetonitrile; ·····, dioxane; – – –, isooctane.

around 284 nm is positive, whereas it becomes negative in nonpolar solvents (Fig. 6).

This small rotational strength at long wave lengths can be ascribed to the decrease of the molecular dissymmetry by introduction of an O atom at the chiral S atom of the corresponding sulphilimine. In addition, the disappearance of the $n \rightarrow \pi^*$ transition of the sulphilimine chromophore by the introduction of an O atom, induces the unusual CD behavior at around 235 nm as compared with that of the corresponding sulphoxide and sulphilimine. In this connection, it is noteworthy that a similar change was observed in the CD behavior of (−)-N-trifluoroacetylsulphilimine (**14**) as described before.

Consequently, the CD measurements did not give the definitive assignment of the configuration at sulphur for the sulphoximine (**16**, **18**). The result is different from the case of (−)-(*R*)-S-methyl S-*p*-tolyl N-*p*-tolylsulphonylsulphoximine, the ORD curve of which is very similar to that of the corresponding (−)-(*S*)-N-*p*-tolylsulphonylsulphoximine and serves as evidence for determining the absolute configuration at sulphur.[12]

Solvent effect on CD curve. The CD Cotton effects for N-unsubstituted sulphilimine (**8**) and sulphoximine (**16**) depend on the nature of the solvent as illustrated in Figs. 5 and 6. The amplitude of Cotton effect for the free sulphilimine (**8**) is larger in nonpolar solvents than in polar media. Similar CD behavior was also found in S-*o*-anisyl S-phenyl N-substituted sulphilimines, sulphoxides and sulphoximines (Table 5). For example, in the (−)-N-acetylsulphilimine (**12**), the amplitudes of the Cotton effects in dioxane are about 2 to 3 times larger than those in methanol. Therefore, the CD changes cannot be accounted for by the intromolecular H-bonding between the O atom of *o*-OMe group and the H atom of the imino group as depicted below. Mislow *et al.* observed a strong solvent effect on the ORD curve of (+)-S-butyl S-methyl sulphoxide and presumed that it is due to the dimerisation

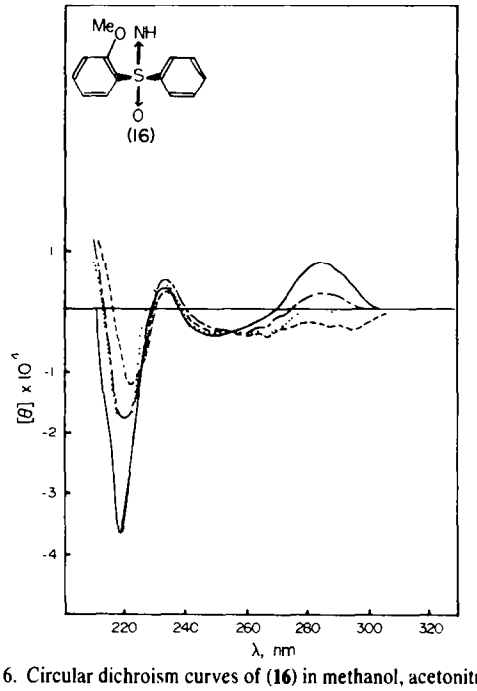
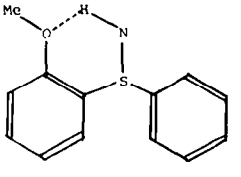


Fig. 6. Circular dichroism curves of (**16**) in methanol, acetonitrile, dioxane and isooctane. ·····, isooctane; – – –, dioxane; ——, methanol; ——, acetonitrile.



16

of the sulphoxide.[27] However, this free sulphilimine (**8**), determined by the freezing point depression method in 0.08 M benzene solution, was confirmed to exist almost in monomer form, in contrast to dialkyl sulphoxides. Therefore, such an association is not responsible for the observed solvent effects.

The most plausible possibility is the solvation. Namely, the relative disposition of the two aryl rings changes by the solute-solvent interaction. Especially, compounds bearing an electron-donating OMe group seems to be proof of such a solvent effect. This is in keeping with the observation that the ORD curve of (−)-S-mesityl S-*p*-tolyl sulphoxide, which has as high an amplitude as that of the *o*-Me derivatives, is quite independent of solvent.[17] Therefore, the dipole–dipole interaction between the polar OMe group and the S–N (or S–O) group is an important factor to determine the optical properties of the *o*-OMe diphenyl chromophore.

Mechanism of the asymmetric synthesis. In order to clarify the stereochemistry of the asymmetric induction, optically active sulphoxides of known absolute configurations were synthesised with the same reaction system. Namely, S-*p*-tolyl S-(*o*-substituted)phenyl sulphoxides were obtained by either thermolysis of the corresponding menthoxysulphonium chloride or alkaline hydrolysis in acetonitrile (Table 6). The former exhibited dextrorotatory (*R*-configuration) while the latter was levorotatory (*S*-configuration), but both had the similar magnitude of rotations. Furthermore, the degree of asymmetric induction is in the following order of the *o*-substituents, i.e. MeO > Me > H, which corresponds to the order of bulkiness. It has been known that the C–O bond cleavage of alkoxysulphonium salt produces the corresponding sulphoxide with retention at the S atom in which the sulphoxide formation by hydrolysis of the salt by alkali proceeds with inversion.[28] Therefore, these observations suggest that the diastereomeric menthoxysulphonium chloride is initially produced in an excess of (*RR*)-form, as illustrated in Scheme 4.

(*S*)-Configurations for all the (−)-sulphilimines obtained by this method were established by the CD measurements as described previously. Thus, in the reaction between the menthoxysulphonium salt and the amide anion, the nucleophilic attack on the S atom by the nitrogen anion occurs with inversion as in the case of the above alkaline hydrolysis (Scheme 4). The optical yields (17–26%) of the sulphilimines (**1**, **5**, **7**) obtained are similar to that of the corresponding sulphoxide (**10**) (22%), and hence the modes of both reactions should be mechanistically analogous.

The stereochemical course of this asymmetric oxidation may be rationalized on the basis of the following arguments: namely, since the *o*-substituent lies close to the isopropyl group of menthyl skeleton in the (*SR*)-salt and that the (*RR*)-salt lies remote, the latter is the sterically favored conformation for the diastereomer, as illustrated in Fig. 7.

EXPERIMENTAL

IR spectra were recorded on a Hitachi 215, NMR spectra on a Hitachi-Perkin Elmer R-20, and CD and UV curves on a JASCO ORD/UV-6. M.ps were uncorrected.

Sulphides. The sulphides were prepared by the decomposition of the diazonium salts of *o*-subsituted anilines in the presence of thiophenol, as described.[29] Their b.ps were 130–135°/2 mmHg for *o*-anisyl phenyl sulphide and 120–125°/2 mmHg for *o*-tolyl phenyl sulphide.

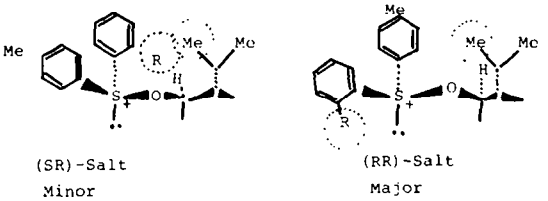
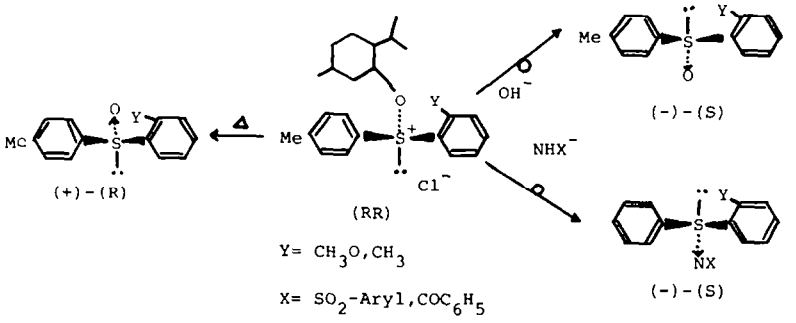


Fig. 7.

Table 6. Sulphoxides obtained from thermolysis and alkaline hydrolysis[a]

R(in p-Tol-S(O)-R)		Yield(%)	$[\alpha]_D$[b]	Confign	O.y.(%)[c]
o-CH_3O	(10)	85(93)	+67.0(-56.1)	R(S)	26(22)
o-CH_3	(11)	88(91)	+13.1(-12.7)	R(S)	15(14)
o-H	(19)	45(70)	0 (0)	-	0(0)

a) The data for sulphoxides obtained from alkaline hydrolysis are shown in parentheses.
b) Determined in acetone (c= ~1.0).
c) The specific rotation of optically pure (S)-(10), (S)-(11) and (S)-(19) are -259°,-89.1° and -21.1° in acetone, respectively.[17]



Scheme 4.

(−)-o-*Substituted diphenyl* N-(*substituted*) *sulphilimines* (**1**, **2**, **3**, **4**, **5**, **6**, **7**) *from sulphides and amide anions*

(A) An equimolar mixture (20 mmol) of a sulphide, (−)-menthol, and pyridine was dissolved in 70 ml of dry acetonitrile and the soln was cooled to −25°. To the soln was added over 20 min with stirring an equimolar amount of t-butyl hypochlorite dissolved in 20 ml of the same solvent. To the above soln, amide anion (22 mmol) (i.e. crystals of sodium arenesulphonamide prepared from the amide and NaOMe in MeOH, or suspension of sodium benzamide in t-BuONa-t-BuOH) was added over 30 min period under vigorous stirring at −25°. The cooling bath was removed while stirring was continued for an additional 10 min. The mixture was poured into dil $Na_2S_2O_3$aq, then was extracted with chloroform. The chloroform layer was shaken with 10% NaOHaq and water, dried over $MgSO_4$ and the solvent was distilled off below 50°. The residue was recrystallised from acetone-hexane (N-arylsulphonylsulphilimines) or benzene-hexane (N-benzoylsulphilimine).

(B) The recrystallisation was repeated two or three times until the specific rotation became constant.

(C) The residue (2 mmol) from the chloroform soln prepared by method (A), was dissolved in 5 ml of acetone, and finely powdered $KMnO_4$ (2 mmol) was added and the whole mixture was stirred for 1 hr at room temp. To the mixture was added 1 ml of MeOH and stirring was continued for 1 hr. The insoluble product of the mixture, after being added into 30 ml of chloroform, was filtered off and the filtrate was washed with water. The soln was dried over $MgSO_4$ and the solvent was distilled off below 50°. Chromatography on silica gel with chloroform gave the pure sulphilimines, which gave identical IR and NMR spectra to those of the authentic samples.

(D) The sulphilimines obtained above were recrystallised from acetone-hexane (N-arylsulphonylsulphilimines) or benzene-hexane (N-benzoylsulphilimine).

(E) The solvent was evaporated from the filtrate after the work up of method (D), and the residue was again recrystallised from the same solvent.

The analytical data, yields and physical properties of the sulphilimines obtained thus are listed in Tables 1 and 7.

(−)-o-*Substituted diphenyl* N-(*unsubstituted*) *sulphilimines* (**8**, **9**)

Compound **1** (4.2 g, 11 mmol) was added step by step over 10 min into 15 ml conc. H_2SO_4 with vigorous stirring at 5°, and stirring was continued for additional 5 min after removing the cooling bath. The resulting light green soln was poured into 300 ml ice-water, and the aqueous soln was filtered after the addition of active charcoal. The acidic soln was made alkaline (pH 10) by addition of 50% NaOHaq together with crushed ice below 5°. The mixture was extracted with three 150 ml portions of benzene. The combined benzene extract was washed with water, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure below 50°. The light yellow oil thus obtained crystallised upon cooling. The product was then recrystallised from benzene-hexane, IR ν_{max} (KBr) 3170 and 930 (907 in CCl_4) cm^{-1}, NMR δ ($CDCl_3$) 1.45 (1H, s, NH), 3.74 (3H, s, o-CH_3O) and 6.86–7.91 (9H, m, aromatic) (Found: C, 67.45; H, 5.59; N, 6.05. Calc. for $C_{13}H_{13}NOS$, C, 67.50; H, 5.66; N, 6.06%). Other physical constants are collected in Table 2. Derivative **9** prepared by a similar treatment gave identical IR and NMR spectra to those of the authentic sample.[30] These free sulphilimines were stored in a refrigerator avoiding moistures, since they are somewhat unstable at room temp.

(−)-S-o-*Anisyl* S-*phenyl* N-*acylsulphilimines* (**7**, **12**, **13**, **14**)

The (−)-free sulphilimine **8** (1 mmol) and dry pyridine (1 mmol) were dissolved in 2 ml dry benzene. Carboxylic acid anhydride (1.2 mmol) in 1 ml of the same solvent was then added over 10 min to the above soln under stirring at 5°. The stirring was continued for 30 min at room temp., and then the mixture was poured into 30 ml chloroform. The soln was shaken with 20% NaOH and then water, and the chloroform layer was dried and evaporated below 50° to yield an oily product, which was chromatographed through silica gel using chloroform as the solvent. The product was recrystallised from benzene-hexane. The derivative **12**; IR ν_{max} (KBr) 1579 and 795 cm^{-1}, NMR δ ($CDCl_3$) 2.21 (3H, s, CH_3); 3.78 (3H, s, o-CH_3O) and 6.84–8.04 (9H, m, aromatic). (Found: C, 65.71; H, 5.45; N, 5.15. Calc. for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12%). The derivative **13**; IR ν_{max} (KBr) 797 and 1577 cm^{-1}, NMR δ ($CDCl_3$) 1.23 (6H, d, $-CH(CH_3)_2$), 3.79 (3H, s, o-CH_3O), and 6.83–8.03 (9H, m, aromatic) (Found: C, 67.98; H, 6.43; N, 4.52. Calc. for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65%). The derivative **14**; IR ν_{max} (KBr) 1640 cm^{-1}, NMR δ ($CDCl_3$) 3.82 (3H, s, o-CH_3O) and 6.90–8.12 (9H, m, aromatic) (Found: C, 55.32; H, 3.76; N, 4.35. Calc. for $C_{15}H_{12}NO_2F_3S$: C, 55.04; H, 3.70; N, 4.28%). The derivative **7** indicated identical IR and NMR spectra to those prepared from the sulphide-amide anion system. Other physical constants are listed in Table 4.

(−)-S-o-*Anisyl* S-*phenyl* N-*β-cyanoethylsulphilimine* (**15**)

The (−)-free sulphilimine **8** (1 mmol) was dissolved in 3 ml acrylonitrile and kept for 22 hr at room temp. An oily product,

Table 7. Analytical, IR and NMR data for N-substituted sulphilimines, o-CH_3O-C_6H_4-S-C_6H_5 (↓ NX)

X		M.p. (°C)	Anal.; Found (Required) C	H	N	ν_{SN} (cm^{-1}) (KBr)	n.m.r.[a] (δ, ppm)
p-$CH_3C_6H_4SO_2$	(1)	161.5–162.0	62.58 (62.31)	4.88 (4.97)	3.64 (3.63)	964	8.18–6.87(m), 3.76(s), 2.35(s)
p-$ClC_6H_4SO_2$	(3)	160.5–161.0	56.45 (56.22)	3.83 (3.97)	3.48 (3.45)	963	8.09–6.86(m), 3.73(s)
p-$CH_3OC_6H_4SO_2$	(4)	149.5–150.5	59.75 (59.83)	4.93 (4.77)	3.52 (3.49)	957	8.11–6.74(m), 3.78(s), 3.73(s)
$C_6H_5SO_2$	(5)	143.5–144.0	61.25 (61.43)	4.47 (4.61)	3.75 (3.77)	967 950[c]	8.13–6.83(m), 3.75(s)
o-$CH_3C_6H_4SO_2$	(6)	153 –154	62.58 (62.31)	4.93 (4.97)	3.55 (3.63)	967	8.20–6.82(m), 3.69(s), 2.60(s)
C_6H_5CO	(7)	118 –119	71.84 (71.62)	4.97 (5.11)	4.27 (4.18)	798	8.40–6.85(m), 3.82(s)
p-$CH_3C_6H_4SO_2$	(2)[b]	122 –122.5	64.69 (65.01)	5.15 (5.18)	3.79 (3.79)	968	7.96–7.05(m), 2.34(s)

a) $CDCl_3$, 60 Mhz (s: singlet, m: multiplet).
b) S-Phenyl S-o-tolyl N-p-tolylsulphonylsulphilimines.
c) Determined in CCl_4.

obtained upon evaporation of acrylonitrile below 40°, was chromatographed through silica gel by elution with $CHCl_3$–MeOH solvent (100:12), and the resulting solids were recrystallised from ether–hexane. IR ν_{max} (KBr) 2240 and 1104 (1091 in CCl_4) cm^{-1}, NMR δ ($CDCl_3$) 2.46(2H, t, $-CH_2CH_2CN$), 3.30(2H, t, $-CH_2CH_2CN$) and 6.9–7.8(9H, m, aromatic) (Found: C, 67.42; H, 5.49; N, 9.79. Calc. for $C_{16}H_{16}N_2OS$: C, 67.58; H, 5.67; N, 9.85%). Other physical constants are collected in Table 4. Since this sulphilimine (**15**) is quite hygroscopic and decomposes gradually even at room temp., it must be stored in a refrigerator, avoiding moisture.

(−)-S-o-*Anisyl* S-*phenyl* N-*arylsulphonylsulphilimines* (**1, 5**) *from the* (−)-*free sulphilimine* (**8**)

The (−)-free sulphilimine **8** (1 mmol) was dissolved in 1 ml dry pyridine. *p*-Toluene sulphonyl chloride (or benzenesulphonyl chloride) (2 mmol) in 1 ml of the same solvent was then added over 10 min to the above stirred soln at 40°. The stirring was continued for 30 min at the same temp., and then the mixture was poured into 30 ml chloroform. The chloroform soln was shaken with 4N HCl and then water, dried over $MgSO_4$. Chloroform was evaporated below 50° to yield a viscous yellow oil, which was chromatographed on silica gel by elution with chloroform. The sulphilimines (**1, 5**) thus obtained were identical in IR and NMR spectra with those prepared by the sulphide-amide anion system. Other physical properties are collected in Table 4.

(+)-S-o-*Anisyl* S-*phenyl* N-(*unsubstituted sulphoximine* (**16**)

Finely powdered $KMnO_4$ (6 mmol) and $MgSO_4$ (6 mmol) were dissolved into 20 ml acetone–water solvent (3:1). The optically pure free sulphilimine **8** (2 mmol), $[\alpha]_D$ −194° (*c* = 1.07, chloroform), in 2 ml acetone was added over 30 min to the above stirred soln at room temp. The stirring was continued for 15 hr. After the addition of 30 ml chloroform, the insoluble materials were filtered off and the filtrate was extracted with 4N HCl. The aqueous soln was made basic (pH 10) by addition of crushed ice and 50% NaOHaq below 5°. The soln was extracted with chloroform. The chloroform soln was washed with water, dried and evaporated. The residual oil was immediately solidfied, (73%), $[\alpha]_D$ +2.4° (*c* = 2.05, chloroform). The product was recrystallised from benzene–hexane, m.p. 132.0–132.5°, $[\alpha]_D$ +2.4° (*c* = 2.13, chloroform), IR ν_{max} (KBr) 3272, 1240, 1123 and 972 cm^{-1}, NMR δ ($CDCl_3$) 3.30 (1H, s, NH), 3.68 (3H, s, *o*-MeO) and 6.78–8.14 (9H, m, aromatic) (Found: C, 63.38; H, 5.25, N, 5.65. Calc. for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30; N, 5.66%).

(−)-S-o-*Anisyl* S-*phenyl* N-p-*tolylsulphonylsulphoximine* (**18**)

The (+)-free sulphoximine **16** (1 mmol), which was derived from the (−)-free sulphilimine **8** ($[\alpha]_D$ −163°) by the method described previously, was dissolved in 1 ml dry pyridine. *p*-Toluenesulphonyl chloride (2 mmol) in 1 ml of the same solvent was added to the above soln. The soln was kept standing for 15 hr at room temp. The pyridine soln was poured onto 30 ml chloroform, and the combined soln was shaken with 4N HCl and then water. The chloroform soln was dried over $MgSO_4$. Chloroform was evaporated to give a viscous oil, which was chromatographed through silical gel using chloroform. The viscous oil (83%) thus obtained was found to be identical to the authentic sample in IR and NMR spectra. $[\alpha]_D$ −101° (*c* = 0.93, chloroform).

(±)-S-o-*Anisyl* S-*phenyl* N-p-*tolylsulphonylsulphoximine* (**18**)

The titled compound was synthesised analogously by the above method, m.p. 149–150° (from acetone–n-hexane), IR ν_{max} (KBr) 1235, 1157, 1075 and 1050 cm^{-1}, NMR δ ($CDCl_3$) 2.37 (3H, s, *p*-CH_3), 3.62 (3H, s, *o*-CH_3O) and 6.77–8.32 (13H, m, aromatic) (Found: C, 60.15; H, 4.79; N, 3.48. Calc. for $C_{20}H_{19}NO_4S_2$; C, 59.83; H, 4.77; N, 3.49%).

(+)-S-o-*Anisyl* S-*phenyl sulphoxide* (**17**)[31]

The (+)-free sulphoximine **16** (1 mmol), $[\alpha]_D$ +2.4° (*c* = 2.13, chloroform), was dissolved in 2M H_2SO_4 (10 ml). $NaNO_2$ (2 mmol) in 2.5 ml water was added over 20 min to the stirred acidic soln at 5°. After the soln was stirred at room temp. for 1 hr, it was made alkaline by addition of crushed ice and solid Na_2CO_3 below 5°. The mixture was extracted with chloroform. The combined extracts were washed with water, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residual oil (95%) was identical to the authentic material in NMR and IR spectra,[32] $[\alpha]_D$ +275° (*c* = 1.03, acetone) and $[\alpha]_D$ +209° (*c* = 1.12, chloroform).

(−)-(S)-*Anisyl* S-*phenyl sulphoxide* (**10**) *and* (−)-(S)-o-*tolyl* S-p-*tolyl sulphoxide* (**11**)

The titled compounds were prepared by the usual procedure as described in the lit.[33] The sulphoxide **10**; $[\alpha]_D$ −223° (*c* = 1.56, EtOH) (lit.[18] $[\alpha]_D$ −221° (EtOH), $[\alpha]_D$ −259° (*c* = 2.12, acetone), and $[\alpha]_D$ −196° (*c* = 1.12, chloroform). The sulphoxide **11**; $[\alpha]_D$ −88.8° (*c* = 1.05, acetone) (lit.[17] $[\alpha]_D$ −89.1° (acetone) and $[\alpha]_D$ −72.8° (*c* = 1.03, chloroform).

Optical active o-*substituted diphenyl sulphoxides* (**10, 11, 19**) *from menthoxysulphonium chlorides by thermolysis or alkaline hydrolysis*

In the first attempt, i.e. thermolysis, the cooling bath was removed from the methylene chloride soln of menthoxysulphonium salt, which was prepared by the method described before, while stirring was continued for 1 hr at 30°. The mixture was shaken with $Na_2S_2O_3$aq and with water, and then dried over $MgSO_4$. After removing of the solvent under reduced pressure, the menthol derivatives were sublimed off. The residue was chromatographed through silica gel using chloroform as an eluent. In the second attempt, i.e. alkaline hydrolysis, the acetonitrile soln of the sulphonium salt was treated slowly with an excess of 10% NaOH aq at −25° with stirring, and then worked up as shown above. The oil thus obtained gave IR and NMR spectra identical to those of the authentic sample.[32] Other physical properties are listed in Table 6.

Cryoscopic measurements on S-o-*Anisyl* S-*phenyl* N-*unsubstituted sulphilimine* (**8**). The apparatus used for performing the cryoscopic experiments and the technique of operating the freezing point measurements are the same as that described in the textbook.[34] The value (4.70°) for molar freezing point depression of 0.08 M benzene solution is of averaged value of three measurements.

CD and UV measurements. The specific rotations (concentration, C: chloroform or A: acetone) at 25° and optical purities (%) of the compounds subjected to the measurements are as follows, (**8**); −64° (*c* = 1.03, C), 33, (**3**); −74° (*c* = 1.04, C), 95, (**4**); −32° (*c* = 1.02, C), 36, (**1**); −95° (*c* = 0.97, C), 97, (**5**); −77° (*c* = 1.01, C), 81, (6); −4.9° (*c* = 1.02, C), could not assigned, (**12**); −74° (*c* = 0.98, C), 47 (7); −74° (*c* = 1.21, C), 97, (**13**); −145° (*c* = 1.04, C), 95, (**14**); −61° (*c* = 0.96, C), 74, (**15**); −61° (*c* = 0.81, C), 45, (**17**); +243° (*c* = 1.02, A), 88, (**10**); −249° (*c* = 2.12, A), 96, (**16**); +2.4° (*c* = 2.13, C), 100, (**18**); −101° (*c* = 0.93, C), 84, (**2**); −6.0° (*c* = 2.32, C), 15, (**11**); −73° (*c* = 1.03, C), 100.

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